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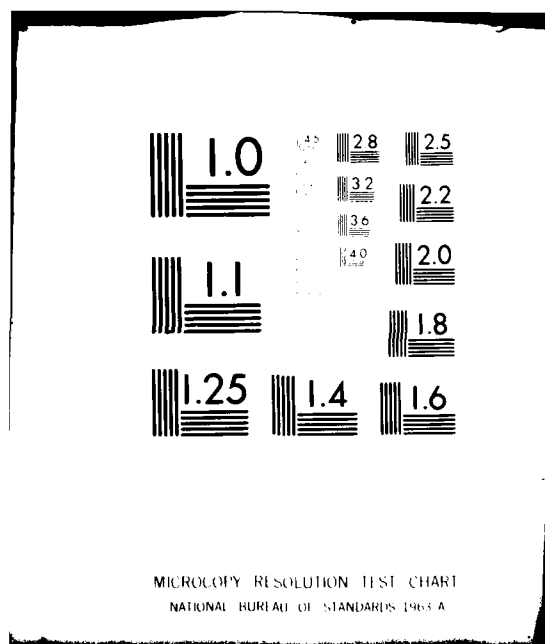
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**SYNTHESIS OF  
ENERGETIC POLYMERS**

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15 July 1979 to 14 July 1980

August 15, 1980

By: J. M. Guimont, G. E. Manser,  
and D. L. Ross

Prepared for:

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20 ABSTRACT (Continued)

3-(2-Fluoro-2,2-dinitroethyl)-3-methyloxetane (FOE) was prepared and polymerized to give oligomers with molecular weights ranging from 6000 to 15000. A complete study of the polymerization of FOE and characterization of the polymers is in progress.

Work on an alternative general route to oxetanes afforded oxetane 3,3-diacetic acid in low yield. Although we anticipated preparation and polymerization of a series of esters based on oxetane diacetic acid, the work was postponed for three reasons: (1) The yield of the acid was much lower than anticipated, (2) esterification did not proceed readily, and (3) under a separate research program, we found that oxetane esters did not polymerize readily.

Work on a general route to nitroalkyl-substituted tetrahydrofurans resulted in 3-(2,2-dinitropropyl) tetrahydrofuran (3-DNP THF) which was prepared using a synthetic route of general applicability to other 3-substituted tetrahydrofurans. Preliminary screening of potential polymerization catalysts resulted in dimer and trimer formation, suggesting that polymerization is possible.

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## SUMMARY

During this first year of the program, three general synthetic routes to the preparation of energetic oxetanes and tetrahydrofurans were investigated.

Efforts to develop a general synthetic route to 3-nitroalkyl-substituted oxetanes starting with methylene malonate were not successful.

3-(2-Fluoro-2,2-dinitroethyl)-3-methyloxetane (FOE) was prepared and polymerized to give oligomers with molecular weights ranging from 6000 to 15000. A complete study of the polymerization of FOE and characterization of the polymers is in progress.

Work on an alternative general route to oxetanes afforded oxetane 3,3-diacetic acid in low yield. Although we anticipated preparation and polymerization of a series of esters based on oxetane diacetic acid, the work was postponed for three reasons: (1) The yield of the acid was much lower than anticipated, (2) esterification did not proceed readily, and (3) under a separate research program, we found that oxetane esters did not polymerize readily.

Work on a general route to nitroalkyl-substituted tetrahydrofurans resulted in 3-(2,2-dinitropropyl) tetrahydrofuran (3-DNP THF), which was prepared using a synthetic route of general applicability to other 3-substituted tetrahydrofurans. Preliminary screening of potential polymerization catalysts resulted in dimer and trimer formation, suggesting that polymerization is possible.



## DISCUSSION

Before starting work on this program, we conducted a thorough literature survey of the preparation and polymerization of oxetanes and tetrahydrofurans. In addition, a parallel program being conducted for the Air Force (AFRPL) provided us with first-hand knowledge of the problems in this research. Based on this background information, two distinct goals were set for the program. This first goal was to synthesize and polymerize an energetic oxetane or tetrahydrofuran to demonstrate the feasibility of the proposed research and to provide a material that could be tested for its applicability to Navy needs.

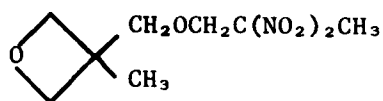
The second goal was to investigate general synthetic routes for the preparation of energetic oxetanes and tetrahydrofurans. It was evident from the literature survey that energetic, polymerizable, 4- and 5-membered cyclic ethers were virtually unknown, and that the few reported ethers were prepared by diverse and difficult synthetic routes. Also, in general, each route provided only one specific monomer as an end product. Because it would be desirable to provide an array of monomers from which to choose, the development of totally new routes to each monomer was considered impractical. Therefore, we investigated the synthesis of energetic cyclic ethers with the objective of producing monomers by routes that could be used later to produce additional monomers as needed.

While attempting to develop a general route to energetic oxetanes, we realized that an immediate solution was not at hand and that additional work was required. Consequently, to provide an energetic polymer as soon as possible that would satisfy Navy requirements, we completed the preparation of FOE (see below) and began its polymerization. Concurrently, a general route to energetic 3-substituted tetrahydrofurans was developed and polymerization of a resultant monomer was partially completed.

## Oxetanes

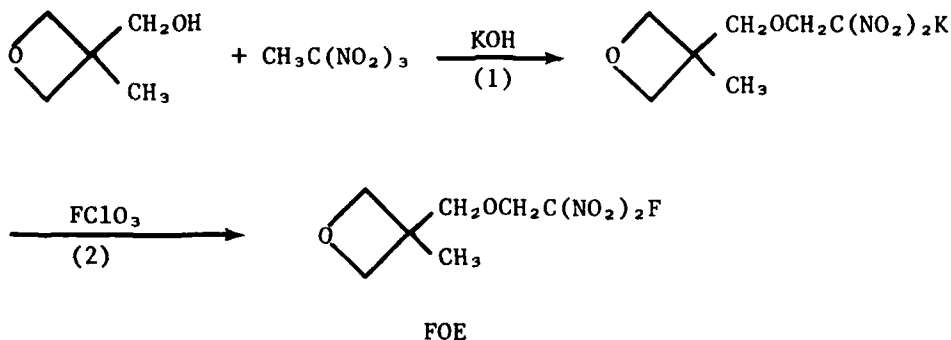
### 3-Methyl-3-(2-fluoro-2,2-dinitroethoxymethyl)oxetane (FOE)

One of the monomers under investigation for AFRPL is Oxether-1.<sup>1</sup>

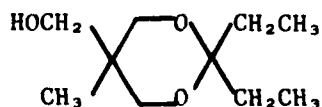


Oxether-1

Oxether-1 polymerizes readily and its synthesis has already been established. Because the presence of fluorine is not acceptable for Air Force low-smoke applications, it was reasonable to modify the route to Oxether-1 to provide the fluorinated analog, FOE. The presence of fluorine not only resulted in a more dense material than Oxether-1, but also increased the oxygen balance. FOE was prepared as shown in Equations (1) and (2).

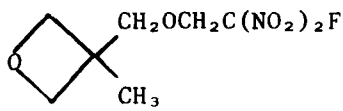


The starting oxetane alcohol was prepared from tris(hydroxymethyl) ethane and diethyl carbonate by formation and pyrolysis of the intermediate cyclic carbonate.



The potassium salt, equation (1), was prepared by the same dinitroethylation procedure used for Oxether-1,<sup>1</sup> and the fluorination with perchloryl fluoride, equation (2), was based on a published procedure.<sup>2</sup> Currently the overall yield of the two reactions is 17%; however, reaction conditions have not been optimized, and alternative methods of fluorination have not been investigated. Details are given in the experimental section. The properties of FOE are shown in Table 1.

Table 1  
PROPERTIES OF FOE

Structure	
Molecular Formula	C <sub>7</sub> H <sub>11</sub> FN <sub>2</sub> O <sub>6</sub>
Formula Weight	238.2
Density (g/cm <sup>3</sup> )	1.365
ΔH <sub>f</sub> (gas) kcal/mol, est.	-183.2

#### Polymerization of FOE

Boron trifluoride etherate was the preferred catalyst for the polymerization of FOE because of its availability and ease of handling and because more is known about boron trifluoride than any other Lewis acid. However, other acceptable Lewis acids used for cationic polymerizations may also be suitable.

Data for five polymerization runs are given in Table 2. For the study, 5 g of FOE monomer was extensively purified by chromatography and dissolved in dry dichloromethane to give a 20% w/w stock solution, which was further dried over molecular sieves before use. Then, 2-g samples of

Table 2

## POLYMERIZATION RUNS FOR FOE

Run	Temperature (°C)	Reactants (parts by weight)			GPC Analysis <sup>a</sup>		Molecular Weight		
		Monomer	BF <sub>3</sub> Et <sub>2</sub> O	H <sub>2</sub> O	Polymer Elution Volume (ml)	% Yield <sup>b</sup>	M <sup>n</sup> (000)	M <sup>w</sup> (000)	Q <sup>d</sup>
1 <sup>c</sup>	20	100	3	0	42	92.3	3.126	6.662	2.13
2	20	100	20	0	43	83.0	-	5.4	-
3	20	100	10	10	52	14.8	-	1.3	-
4	20	100	10	1	43.5	82.0	-	5.0	-
5	40	100	10	1	43.8	87.6	-	4.4	-

<sup>a</sup>Analyzed using a Waters Associates GPC with THF on microstyragel columns (two 100 Å, two 500 Å, one 10<sup>-3</sup> Å, one 10<sup>-4</sup> Å, one 10<sup>-5</sup> Å).

<sup>b</sup>The balance of recovered material was unreacted monomer (elution volume: 61.5 ml).

<sup>c</sup>Analysis by Chromatix KMX6 light scattering analyzer attached to the effluent. All other molecular weights determined by comparison to polypropyleneglycol standards.

<sup>d</sup>Polydispersity,  $Q = \frac{M^w}{M^n}$ .

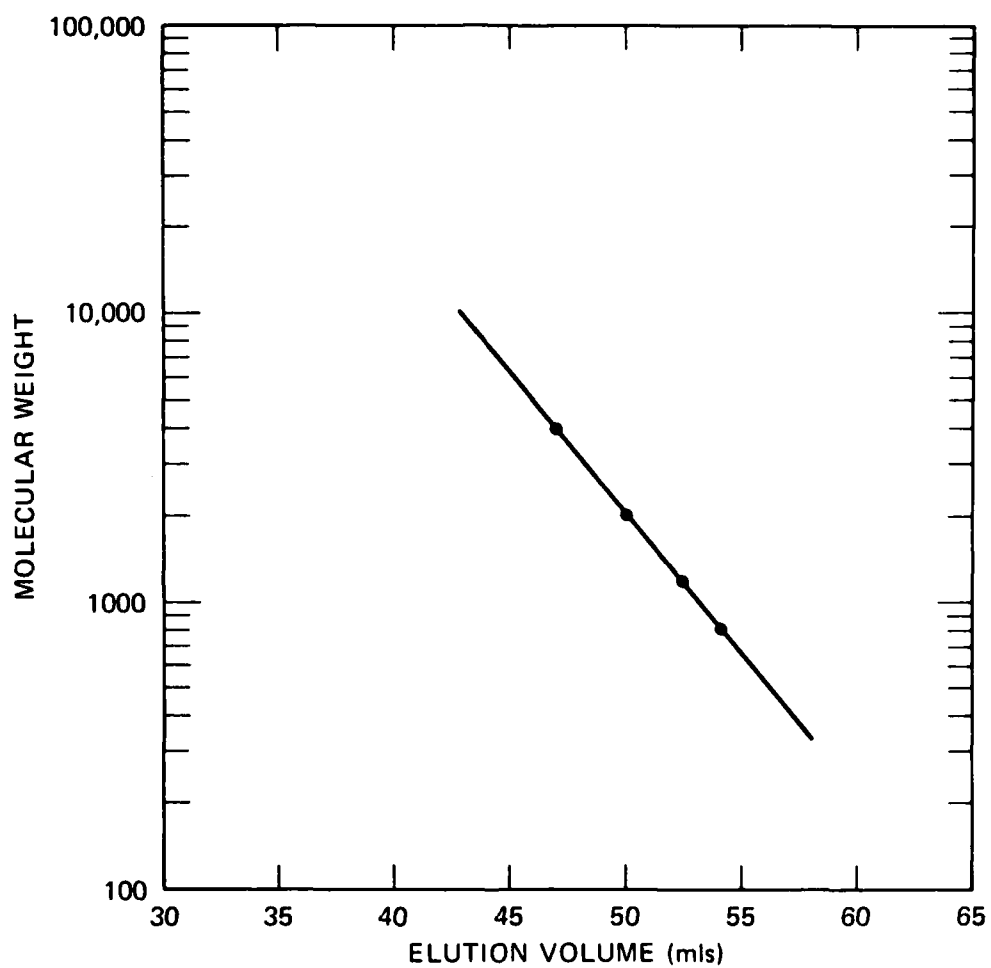
the stock solution (400 mg monomer) were withdrawn and placed in a flame-dried reactor under nitrogen and the catalyst/cocatalyst was introduced. After a reaction time of 180 min, the polymerization was quenched with brine and organic soluble products were analyzed by gel permeation chromatography. This technique afforded better than 95% weight recovery in all five runs.

Our GPC system is a set of seven microstyrogel columns (two 100-Å, two 500-Å, one 10<sup>3</sup>-Å, one 10<sup>4</sup>-Å, and one 10<sup>5</sup>-Å). They were calibrated with a set of polypropylene glycol (PPG) standards, and the plot of log MW versus elution volume is shown in Figure 1.

Run 1 was used as a starting point for catalyst loading to obtain relatively low molecular weight products. We hoped to lower the molecular weights of the resulting polymers by increasing the catalyst loading, using water as a cocatalyst, and raising the polymerization temperature, since all these parameters effectively increase the competing termination reactions that occur during chain extension. Apparently only run 3, using an equal amount of catalyst to water, had a noticeable effect on decreasing the polymer molecular weight; however, it also had a detrimental effect on the yield of the polymer, and in fact, almost 80% of the monomer was recovered. Except for this run, the molecular weights of the polymers obtained were in the range of 5,000 to 6,000 and had the appearance of a clear viscous syrup. The GPC data also showed that a significant amount of a component tentatively identified as the cyclic tetramer was produced, but it can be removed from the polymer by treatment with methanol and water.

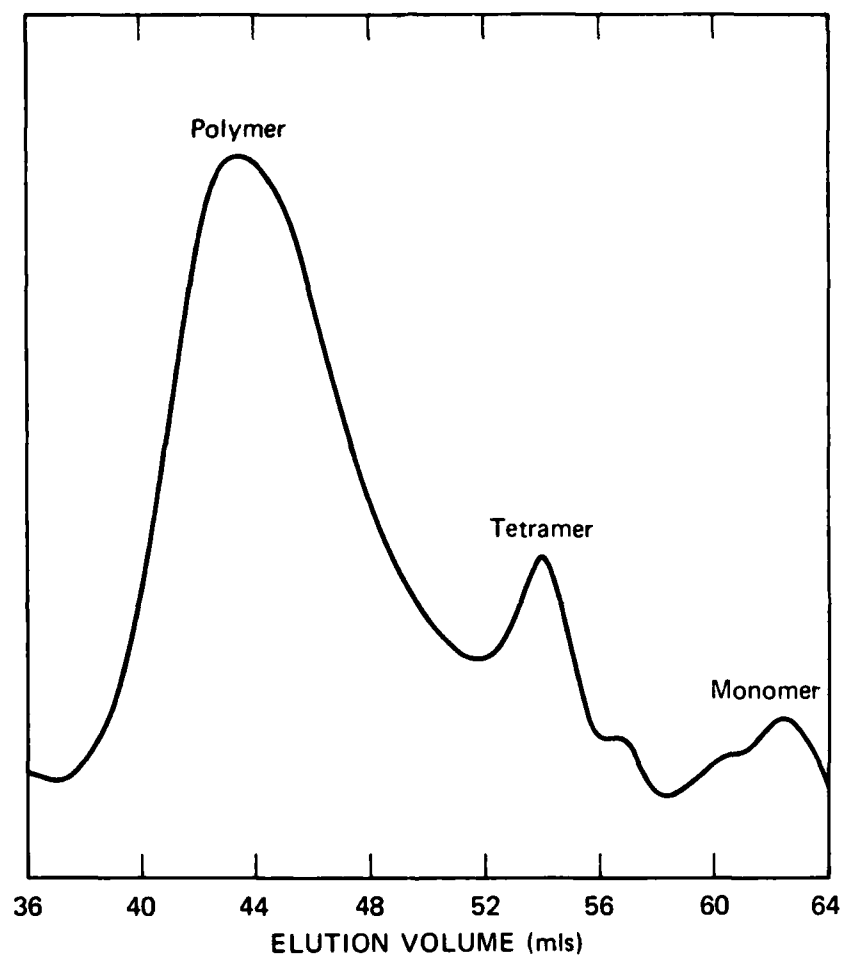
A typical GPC is shown in Figure 2. The polymer has a measured density of 1.394, but the sample used was contaminated with monomer and tetramer. A pure polymer is expected to have a somewhat higher density.

The availability of the monomer did not allow large enough quantities of the polymer to be produced for functionality analysis at this time, however, this investigation showed that polymers having reproducible, narrow molecular weight distributions can be obtained.



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FIGURE 1 GPC CALIBRATION PLOT

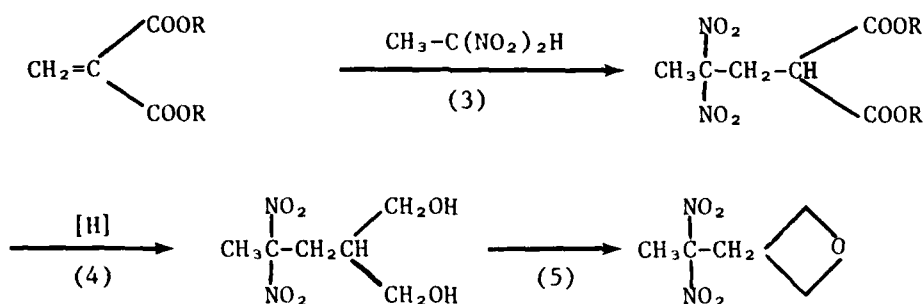


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FIGURE 2 GPC OF FOE POLYMERIZATION

### 3-(2,2-Dinitropropyl)oxetane

The first of two general synthetic routes to nitroalkyl-substituted oxetanes is shown in equations (3) to (5). The first target monomer was 3-(2,2-dinitropropyl)oxetane, but a number of other monomers could be prepared by replacing dinitroethane with any of several other 1,1-dinitroalkanes.



Methylene diethyl malonate was prepared in high yield by the method of Bachmann and Tanner<sup>3</sup> and purified by vacuum distillation. Its reaction with dinitroethane in the presence of triethyl amine, equation (3), as described by Kloetzel<sup>4</sup> was found to produce 2-(2,2-dinitropropyl)diethyl malonate almost quantitatively.

An extensive study of the chemical reduction of this ester was then undertaken. Lithium borohydride in the THF at room temperature and at reflux was found to have little effect and even sodium borohydride-aluminum chloride in diglyme, which is considered to be a very effective reducing agent for esters in the presence of nitro groups, was found to be ineffective (even at 75°C). Diborane under increasingly vigorous conditions also had no effect. A possible cause for the failure of this reduction is the keto-enol tautomerism, which malonate esters are known to undergo readily.



It was then considered more expedient to examine the hydrolysis of the ester to the dicarboxylic acid followed by reduction to the diol with diborane. Only acid hydrolysis of the ester was attempted because of the presence of the nitro group, which would be decomposed by strong base. When hydrolysis was attempted in hydrochloric acid, it was found that rapid decarboxylation followed hydrolysis until the hydrochloric acid concentration was reduced to 5%,<sup>5,6</sup> at which point only unconverted ester was recovered. Examination of the literature showed that diethyl malonate was reported<sup>7</sup> to be readily hydrolyzed to malonic acid in the presence of 0.1% sulfuric acid. This procedure was followed using sulfuric acid concentrations from 0.1% to 10%, but only the unreacted ester was recovered. It appears that even hydrolysis may be hindered by keto-enol tautomerism.

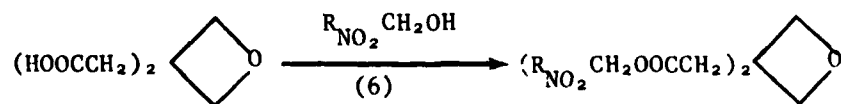
A recent method by Olah<sup>8,9</sup> and Tse Lok Ho,<sup>10</sup> involving trans-esterification by hexamethyldisilane followed by hydrolysis with ice water, was used, but on workup no identifiable product was isolated.

Since literature information suggested that the methyl ester might be hydrolyzed more readily than the ethyl ester, the hydrolysis procedures were repeated using the dimethyl ester; the same results were obtained. As a final effort to obtain the diol, we attempted to convert the ester to the amide and then hydrolyze the amide. Diethylmalonate is readily converted to the amide by reaction in liquid ammonia using a catalytic amount of ammonium chloride.<sup>9</sup> This procedure was followed, but the required amide was not isolated on workup.

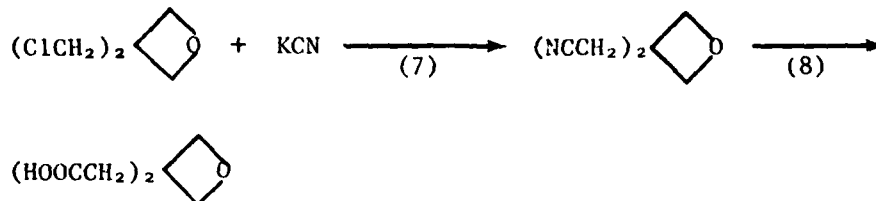
In view of the difficulties encountered during this investigation, no further work in this area is planned.

#### Oxetane 3,3-Diacetic Acid

The second general route to energetic oxetanes that we investigated required synthesis of oxetane 3,3-diacetic acid as an intermediate for esterification with energetic alcohols, equation (6).



Our initial investigation of the synthesis of oxetane diacetic acid was based on the reported procedure<sup>12</sup> as shown in equations (7) and (8).



Conversion of bis(chloromethyl)oxetane to the bis-nitrile, equation (7), proceeded in good yield, but we were unable to repeat the reported<sup>\*</sup> hydrolysis of the nitrile to the diacid with barium hydroxide. Therefore, we investigated a second method<sup>13</sup> using potassium hydroxide and hydrogen peroxide. Oxetane diacetic acid was isolated from the hydrolysis reaction mixture only with great difficulty because of the extreme solubility of the free acid in water. During the workup, a significant amount (relative to the free acid) of the anhydride of the desired product was also obtained. Because the preferred procedure for esterification, equation (6), involves the use of dicyclohexylcarbodiimide (DCC), and because DCC promotes anhydride formation, the probability of obtaining a good yield of ester was very low owing to the propensity of the acid to form anhydride. Therefore, the procedure was not attempted. Instead, we attempted to prepare the bis(fluorodinitroethyl) ester by a procedure reported<sup>14</sup> for esterification of malonic acid with fluorodinitroethanol in trifluoroacetic acid. None of the desired product was detected.

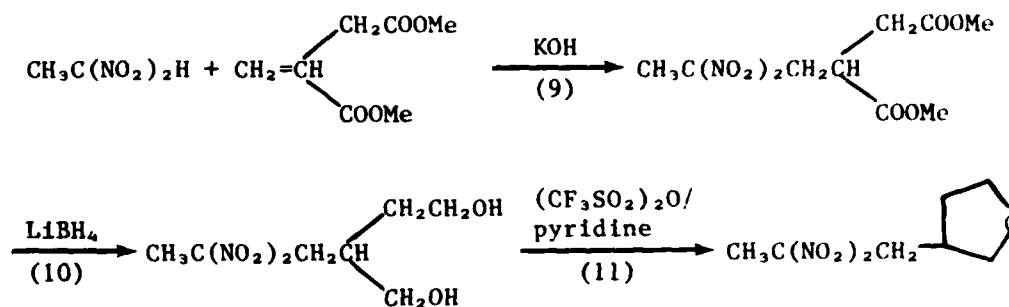
Investigation of the polymerization of oxetane esters under our Air Force contract has revealed that polymerization of oxetane esters with boron trifluoride proceeds slowly and in low conversion compared to other substituted oxetanes. Because oxetane diacetic acid did not esterify readily and the ester may not polymerize well even if formed, work on this synthetic scheme was abandoned in favor of more productive areas of investigation.

<sup>\*</sup> Since we were unable to obtain a copy of the original paper, our work on the hydrolysis was based on the abstract of a Belgian journal as given by Chemical Abstracts.

## Tetrahydrofurans

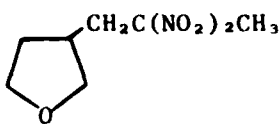
### 3-(2,2-Dinitropropyl) Tetrahydrofuran (3-DNPTHF)

The general route for synthesis of energetic tetrahydrofurans, equations (9) to (11), parallels the route used for synthesis of oxetanes. Synthesis of substituted tetrahydrofurans is described extensively in the literature and several alternative methods for ring closure are available. Although nitroalkyl-substituted tetrahydrofurans can be prepared more easily than oxetanes, we restricted our investigation to this one route because of anticipated polymerization difficulties. Only 3-methyl and 2-methyl tetrahydrofuran have been polymerized and then only with great difficulty. Until polymerization of substituted tetrahydrofurans is better understood, additional synthetic work on monomers is not justifiable.



Addition of dinitroethane to dimethyl itaconate, equation (9), was successfully carried out using potassium hydroxide as a catalyst, and reduction of the ester with lithium borohydride, equation (10), yielded the diol. The ring closure, equation (11), using trifluoromethane sulfonic anhydride and pyridine, yielded 3-(2,2-dinitropropyl) tetrahydrofuran, which is a colorless oil. Details of the procedure are given in the experimental section, and the properties of 3-DNPTHF are given in Table 3.

Table 3  
PROPERTIES OF 3-DNP THF

Structure	
Molecular Formula	C <sub>7</sub> H <sub>12</sub> N <sub>2</sub> O <sub>5</sub>
Formula Weight	204.2
Density (g/cm <sup>3</sup> )	1.305
ΔH <sub>f</sub> (gas) kcal/mol, est.	-111.65

#### Polymerization of 3-DNP THF

Work was initiated by a careful screening of catalysts for the homopolymerization of 3-DNP THF. The catalysts chosen were chlorosulfonic acid,<sup>15</sup> trifluoromethanesulfonic anhydride,<sup>16</sup> boron trifluoride etherate,<sup>17,18</sup> and fluorosulfonic acid,<sup>19</sup> based on their reported uses as catalysts for the homopolymerization of tetrahydrofuran and 3-methyl tetrahydrofuran. Most of these catalysts had also been used in conjunction with cocatalysts such as water, acetic acid, and epichlorohydrin to form relatively low molecular weight products (2,000) with a reported functionality of 2.

Because of the lower reactivity ratio of the monomer and the ceiling temperature of THF polymerizations, runs were conducted at -20°C and over extended reaction times (up to 14 days). The runs were quenched with brine, and GPC analysis was conducted on the residues. Chlorosulfonic acid was found to convert 25% of the monomer to an oligomer with a molecular weight approximating the trimer. It is reported by Hellmann<sup>20</sup> that the reactivity ratio of THF is 1.51 and that for 3-methyl, THF is 0.16, therefore, longer reaction times will be required for homopolymerization

of 3-DNP THF. We plan to conduct further work on this system by varying reaction times and temperatures. In the short term, however, it is possible that 3-DNP THF could be used as a comonomer or cocatalyst based on the work of Tsuda,<sup>21</sup> Saegusa,<sup>22</sup> and Hubin.<sup>16,17</sup> Work is now under way on these copolymerization systems.

## EXPERIMENTAL DETAILS

The experimental procedures reported below are either new synthetic reactions that are not reported in the literature or are significantly modified versions of known reactions. All other experiments reported in the text are a duplication of published procedures.

### Dimethyl 2-(2,2-dinitropropyl)-1,4-butanedioate

A mixture of 155 g (1.3 mol) 1,1-dinitroethane, 205 g (1.3 mol) dimethyl itaconate, 20 ml 20% aqueous sodium hydroxide, 250 ml water, and 500 ml methanol was refluxed for 5 days. The reaction mixture was cooled, and the lower organic phase was separated. The aqueous phase was extracted with 500 ml of methylene chloride; this was combined with the organic phase, washed with 5% sodium bicarbonate, dried over magnesium sulfate, and evaporated. The product was 267 g of a dark oil (75% yield) that crystallized on standing. This product was used without further purification.  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  2.2 (s,  $\text{CH}_3\text{CNO}_2$ ), 2.75 (d,  $J = 7$  Hz), 3.2 (m, CH), 3.7 (s,  $\text{CH}_3\text{O}$ ), 3.75 (d,  $\text{CH}_2\text{CNO}_2$ ,  $J = 7$  Hz)

### 2-(2,2-Dinitropropyl)-1,4-butanediol

A solution of 32 g (0.12 mol) of dimethyl 2-(2,2-dinitropropyl)-1,4-butanedioate in 400 ml THF was added to a mixture of 7 g (0.32 mol) of lithium borohydride in 700 ml THF at  $23^\circ\text{C}$  over a period of 1 hour. The reaction mixture was stirred for an hour at  $25^\circ\text{C}$ , and 50 ml of water was added cautiously. The mixture was reduced to 100 ml volume on a rotary evaporator and then diluted to 200 ml with water. This solution was extracted with ether to give 20 g crude product in 75% yield. This product was used without further purification.  $^1\text{H}$  nmr ( $\text{CDCl}_3$ )  $\delta$  1.7 (m,  $\text{CH}_2\text{C}$ ), 2.2 (s,  $\text{CH}_3$ ), 2.6 (m, CH), 3.7 (m,  $\text{CH}_2\text{OH}$ ,  $\text{CH}_2\text{NO}_2$ ).

### 3-(2,2-Dinitropropyl) Tetrahydrofuran (3-DNP THF)

A solution of 25.4 g (0.09 mol) trifluoromethane sulfonic acid in 400 ml ether was added to a mixture of 20 g (0.09 mol) of 2-(2,2-dinitropropyl)-1,4-butanediol, 7.1 g (0.09 mol) pyridine, and 500 ml ether at 25°C over a period of 1 hour. After stirring an additional hour at 25°C, the ether solution was decanted, washed with 5% sodium bicarbonate, and dried with magnesium sulfate. The ether solution was evaporated, and the crude product was chromatographed on silica gel with methylene chloride as eluent to give 3.4 g pure product in 19% yield. <sup>1</sup>H nmr (CDCl<sub>3</sub>) δ 2.15 (s, CH<sub>3</sub>), 2.64 (d, CH<sub>2</sub>CNO<sub>2</sub>, J = 6 Hz), 3.3 (m, CH<sub>2</sub>CH), 3.8 (m, CH<sub>2</sub>OCH<sub>2</sub>). Elemental anal. calcd. for C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>: C, 41.17; H, 5.88; N, 13.72. Found: C, 41.09; H, 6.00; N, 13.64.

### 3,3-Bis(cyanomethyl)oxetane

To 50 g bis(chloromethyl)oxetane (0.323 mol) dissolved in 200 ml ethyl alcohol was added 34 g sodium cyanide (0.694 mol), and the resulting suspension was heated to reflux for 18 hours. Filtration of the deep-red solution yielded 40 g (0.69 mol) sodium chloride. Further purification of the required product was found to lead to decomposition; hence, the ethyl alcohol was carefully removed and the viscous product was stored under nitrogen at 0°C until used.

### Oxetane 3,3-diacetic Acid

In 200 ml 30% potassium hydroxide was dissolved 36.2 g bis(cyanomethyl)oxetane. Then with vigorous stirring, 72 ml of 30% hydrogen peroxide was added dropwise at a rate so that the temperature did not exceed 60°C. After complete addition the reactor was purged with nitrogen and the reactants were warmed to 75°C. A strong evolution of ammonia gas was detected, but this ceased after 16 hours. The clear orange solution was then cooled to room temperature and extracted with 200 ml diethyl ether. The aqueous solution was held at 20°C and acidified to pH 2.0 with concentrated hydrochloric acid. The resultant solution was then continuously extracted with ether for 2 weeks. The ether extract was

evaporated to dryness, yielding 5.1 g of a viscous oil. From this product was recovered 3.7 g of white solid, which was shown to be the cyclic anhydride by elemental and infrared analysis, and 1.4 g of oil, which slowly crystallized. Elemental analysis and titration against base showed that the oil was the required oxetane 3,3-diacetic acid.

Anhydride anal. calcd. for  $C_7H_8O_4$ : C, 53.85; H, 5.12.

Found: C, 53.41; H, 5.21.

Acid anal. calcd. for  $C_7H_{10}O_5$ : C, 48.27; H, 5.74.

Found: C, 48.01; H, 5.57.

### 3-Methyl-3-(potassium 2,2-dinitroethoxymethyl)oxetane

Potassium hydroxide (6.6 g; 0.1 mol) was dissolved in 30 g 3-methyl-3-hydroxymethyloxetane by stirring at 50°C for 18 hours. This solution was cooled and mixed with 100 ml ether to facilitate stirring. To this mixture was added a solution of 8.25 g (0.05 mol) of trinitroethane in 50 ml ether at 25°C over a period of 1 hour. The reaction mixture was refluxed for 2 hours, cooled, and filtered. The filtered salt was washed with ether and air dried, and was used in the subsequent fluorination without purification.

### 3-Methyl-3-(2-fluoro-2,2-dinitroethoxymethyl)oxetane (FOE)

A mixture of 6.33 g (0.025 mol) of 3-methyl-3-(potassium 2,2-dinitroethoxymethyl)oxetane in 70 ml methanol was placed in a flask fitted with a gas inlet over the liquid surface and dry ice/acetone condenser. The flask was purged with nitrogen and perchloryl fluoride was added at such a rate as to maintain a slow reflux for 2 hours. After adding 70 ml of water to the flask, the mixture was extracted with methylene chloride. The methylene chloride solution was dried and evaporated, leaving a crude product. Chromatography on silica gel with methylene chloride showed the product was 1.0 g of pure FOE in 17% yield.  $^1H$  nmr ( $CDCl_3$ )  $\delta$  1.28 (s,  $CH_3$ ), 3.77 (s,  $CH_2O$ ), 4.41 (s,  $CH_2$  ring), 4.65 (d,  $CH_2F$ ,  $J = 17$  Hz).



#### FOE Polymerization (Typical Reaction)

A 20% w/w stock solution of monomer in methylene chloride was prepared and dried over molecular sieves. Boron trifluoride etherate was distilled and stored under nitrogen before use. Then 2 g of the monomer stock solution (400 mg monomer) was charged into a flame-dried reactor under nitrogen at room temperature. Boron trifluoride etherate catalyst was added dropwise and the polymerization was allowed to continue for 3 hours. The solution was quenched with 0.5 ml saturated aqueous sodium chloride solution and the organic layer was removed and dried over magnesium sulfate. After filtration and evaporation to constant weight, the resultant oil was analyzed by gel permeation chromatography.

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